Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


# Electronic Supplementary Information

## σ-Hole···π and Lone Pair···π Interactions in Benzylic Halides

*Teresa Montoro, Gloria Tardajos, Andrés Guerrero, María del Rosario Torres, Cástor Salgado, Israel Fernández* and José Osío Barcina**

*Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, (Spain)*

E-mail: josio@quim.ucm.es, israel@quim.ucm.es

**Contents**

## X-Ray data collection and structure refinement

Data collection for **1,** was carried out at room temperature on a Bruker Smart CCD diffractometer and on a Xcalibur, Atlas CCD difractometer for **2** and **3**, using in all cases graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) operating at 50 kV and 20 mA for **1** and at 50 kV and 40 mA for **2** and **3.** The exposure times were 20s for **1** and 6.0s and 17.10s **2** and **3** in omega. A summary of the fundamental crystal and refinement data is given in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares procedures on $F^2$ (SHELXL-97)*. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in their calculated positions and refined riding on the respective carbon atoms.

"CCDC 1007894-1007896 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif."

*G.M. Sheldrick, 'SHELX97, Program for Refinement of Crystal Structure', University of Göttingen, Göttingen, Germany, 1997

Table 1. Crystal data and Refinement Data for **1**, **2** and **3**.

| Crystal Data | **1** | **2** | **3** |
|---|---|---|---|
| empirical formula | $C_{13}H_{15}I$ | $C_{13}H_{15}Br$ | $C_{13}H_{15}Cl$ |
| formula wt | 298.15 | 251.16 | 206.70 |
| crystal system | Monoclinic | Monoclinic | Monoclinic |
| space group | P2(1)/n | P2(1)/n | P2(1)/n |
| *a*/Å | 6.350(5) | 6.201(5) | 6.3915(4) |
| *b*/Å | 31.01(3) | 30.714(5) | 6.8582(5) |
| *c*/Å | 6.458(5) | 6.350(5) | 24.607(2) |
| $\alpha$/° | 90 | 90 | 90 |
| $\beta$/° | 112.53(1) | 114.351(5) | 94.259(7) |
| $\gamma$/° | 90 | 90 | 90 |
| *V*/Å$^3$ | 1175(2) | 1102(1) | 1075.7(1) |
| Z | 4 | 4 | 4 |
| $D_c$ /g/cm$^3$ | 1.686 | 1.514 | 1.276 |
| $\mu$(Mo-Kα) /mm$^{-1}$ | 2.687 | 3.688 | 0.311 |
| F(000) | 584 | 512 | 440 |
| $\theta$ range/° | 1.31 to 25.00 | 3.58 to 25.01 | 3.32 to 25.01 |
| index ranges | -7,-36,-7 to 5, 33, 7 | -5,-36,-7 to 7, 36, 6 | -7,-6,-29 to 7, 8, 25 |
| reflections collected | 6319 | 4416 | 4401 |
| unique reflections [Rint] | 2055 [Rint = 0.1078] | 1866 [R(int) = 0.0247] | 1891 [R(int) = 0.0356] |
| completeness to theta | 98.7% | 95.7% | 99.8% |
| data/restraints/params | 2055 / 0 / 127 | 1866 / 0 / 127 | 1891 / 0 / 127 |
| Goodness-of-fit on $F^2$ | 0.997 | 0.997 | 0.998 |
| R1 (reflns obsd) [I>2$\sigma$(I)] [a] | 0.0442 (1483 ) | 0.0360 (1474) | 0.0439 (1343) |
| *w*R2 (all data) [b] | 0.1018 | 0.0865 | 0.0959 |

[a] $R1=\Sigma||F_o|-|F_c||/\ \Sigma|F_o|$ [b] $wR2=\{\Sigma[w(F_o^2-F_c^2)^2]/\ \Sigma[w(F_o^2)^2]\}$

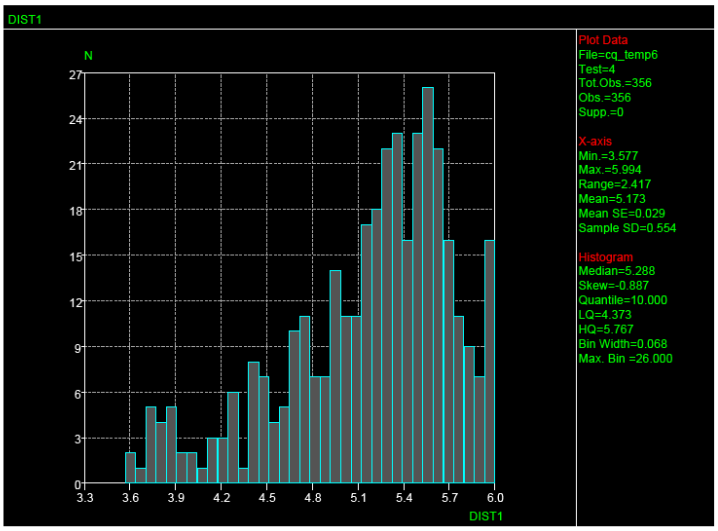



**Figure S1** Histogram from a CSD search representing the intermolecular I···π (phenyl centroid) distance in benzylic iodides.

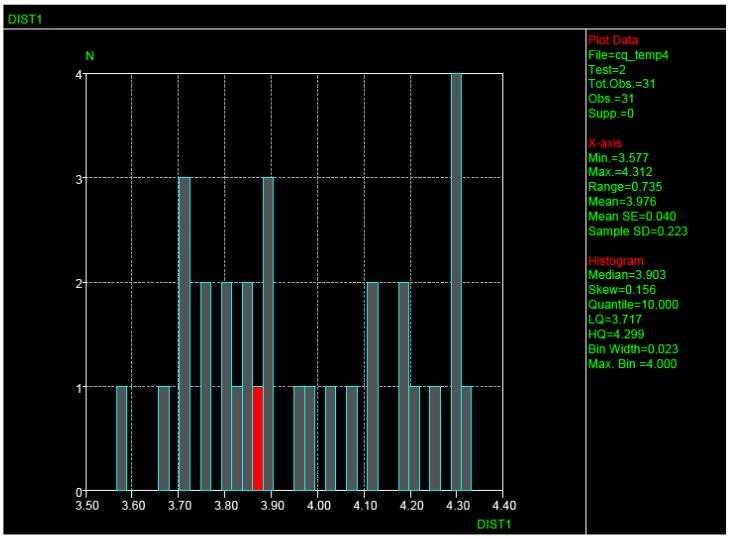



**Figure S2** Histogram from a CSD search representing the intermolecular I···π (phenyl centroid) distance in benzylic iodides in the region around the sum of the corresponding van der Waals radii (3.85 ± 0.5 Å).

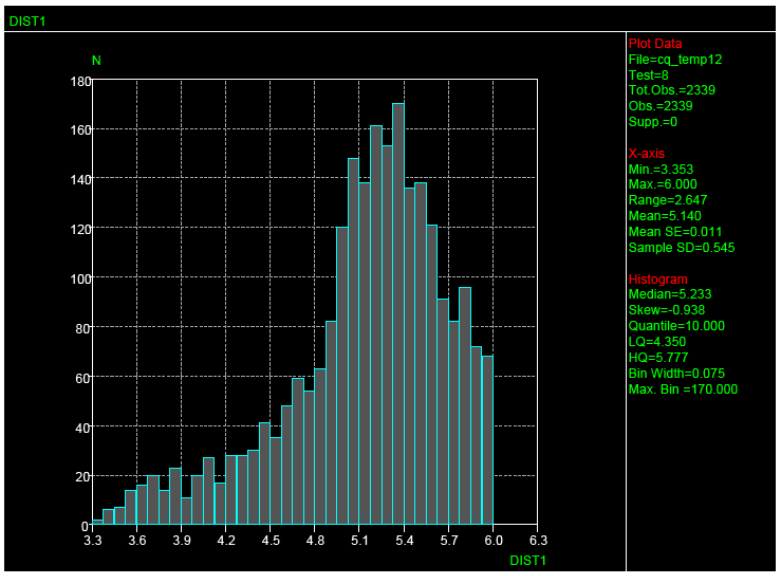



**Figure S3** Histogram from a CSD search representing the intermolecular Br···π (centroid) distance in benzylic bromides.

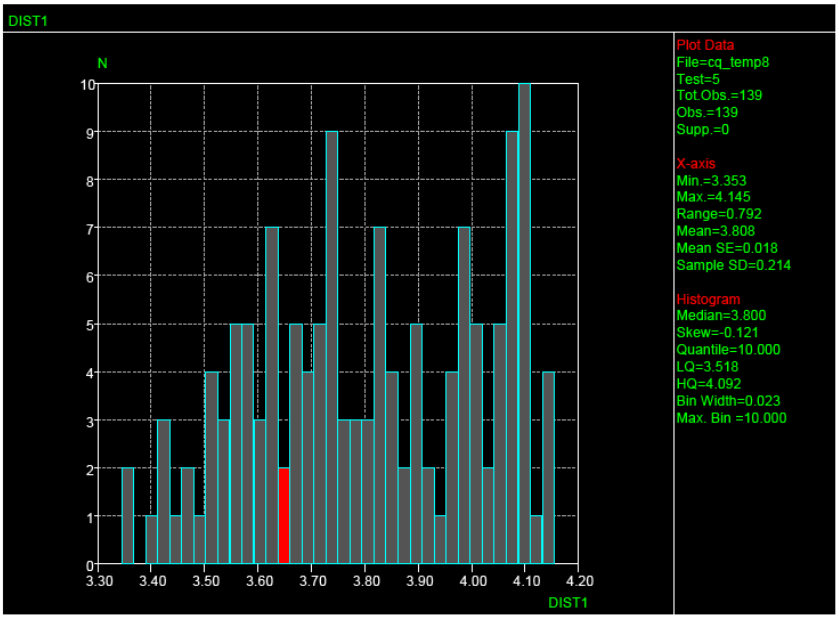



**Figure S4** Histogram from a CSD search representing the intermolecular Br···π (phenyl centroid) distance in benzylic bromides in the region around the sum of the corresponding van der Waals radii (3.65 ± 0.5 Å).

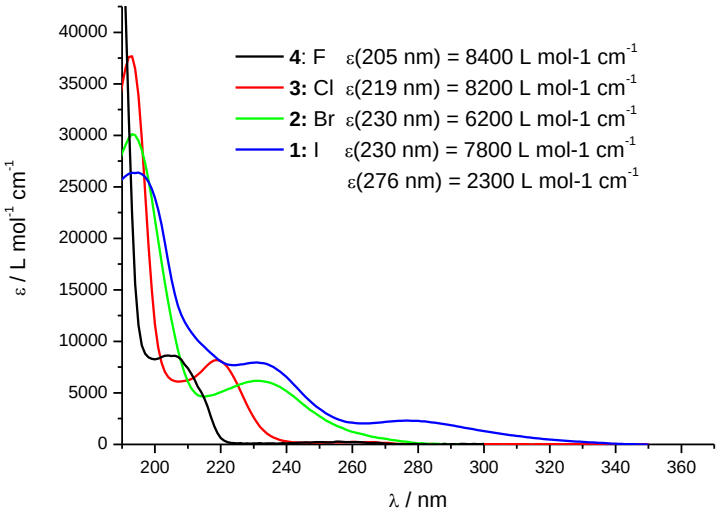



**Figure S5** UV-Vis spectra of benzylic halides **1**-**4** showing the $\beta$ (or $^1B_b$) bands.

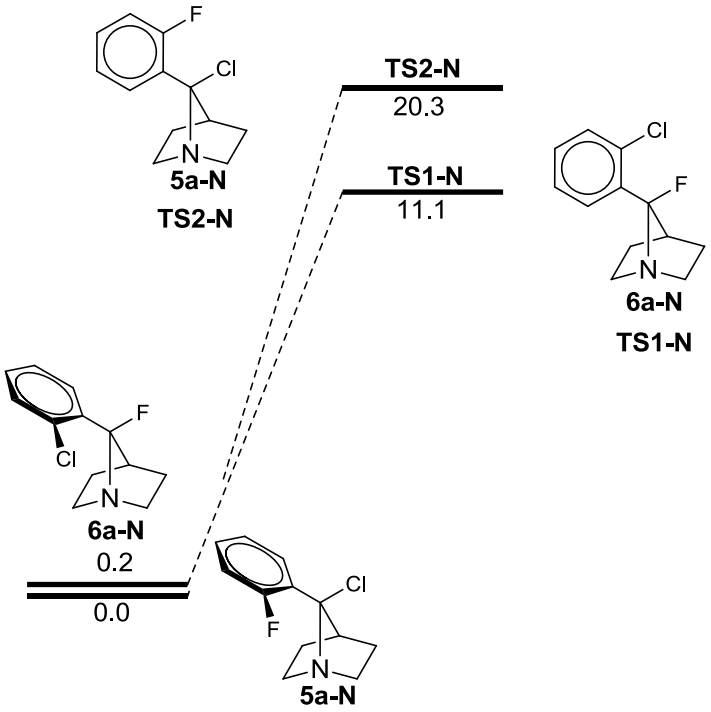
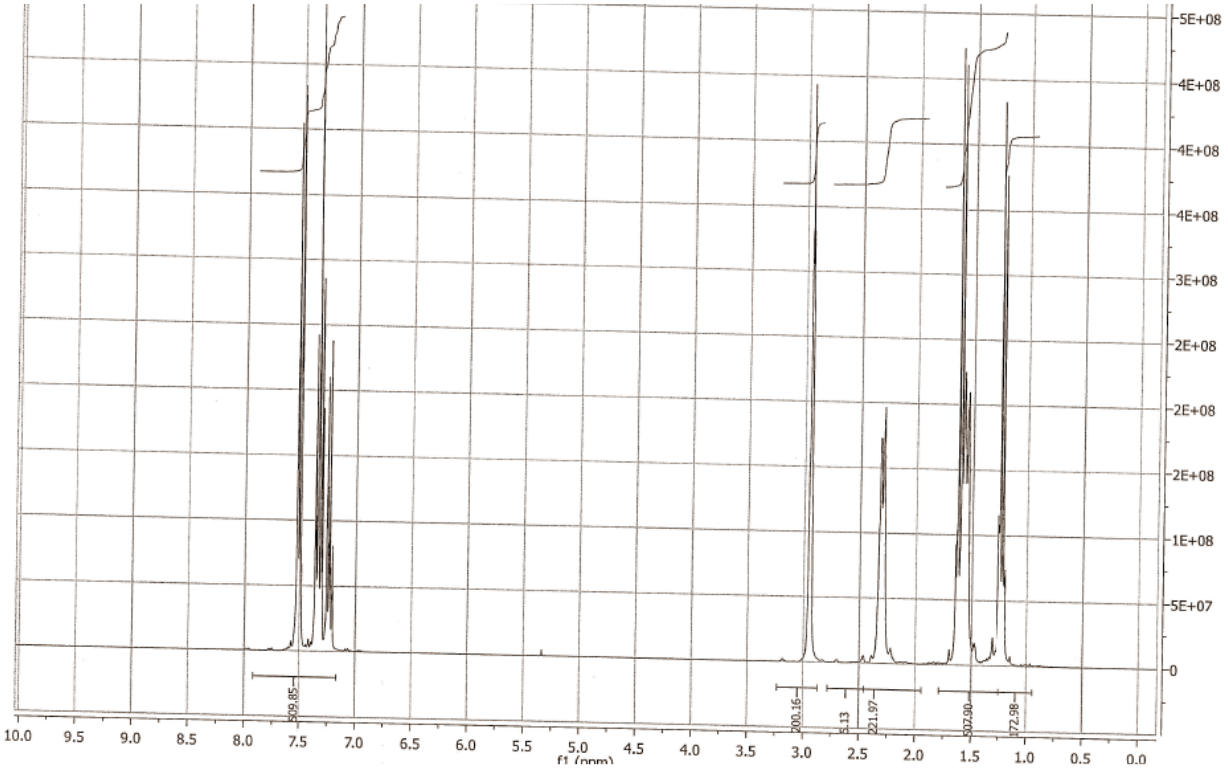
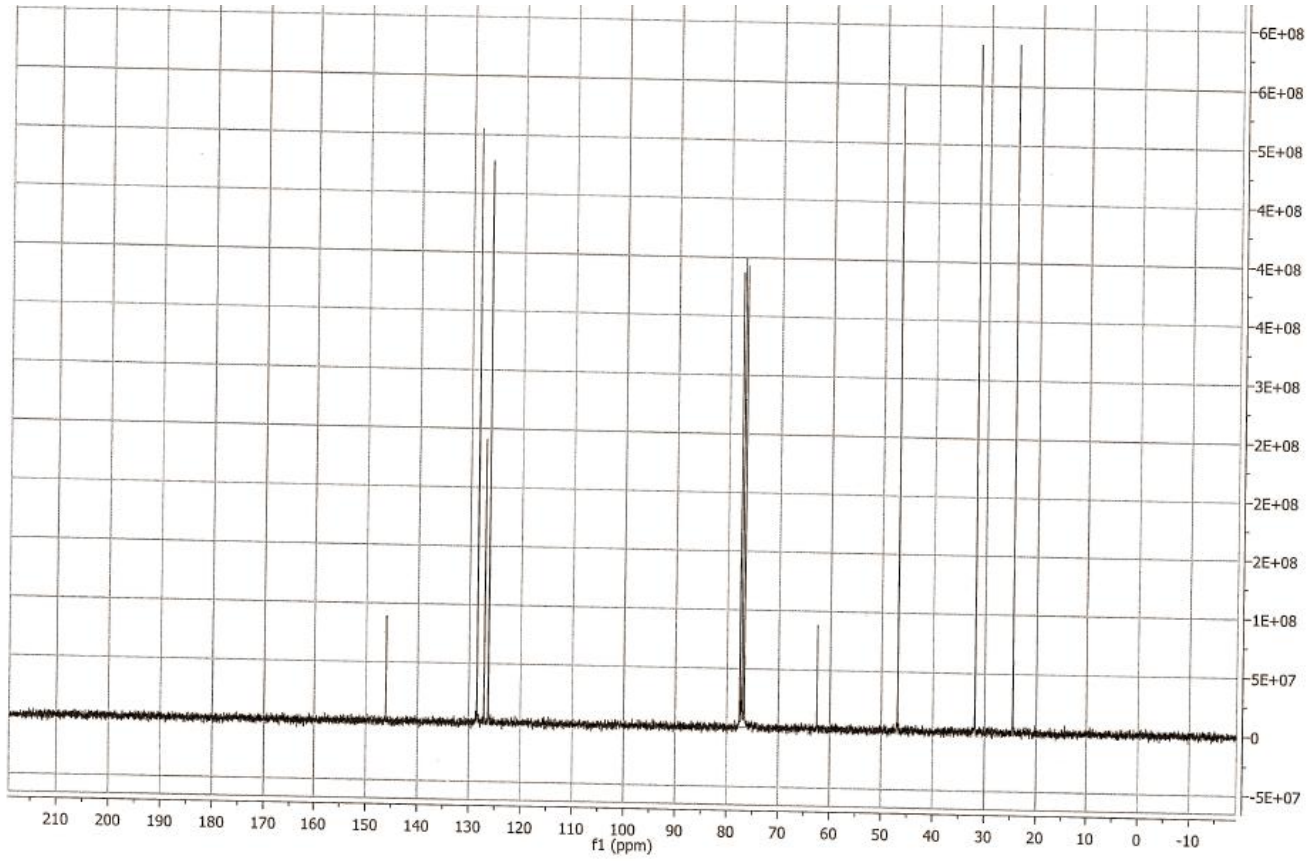


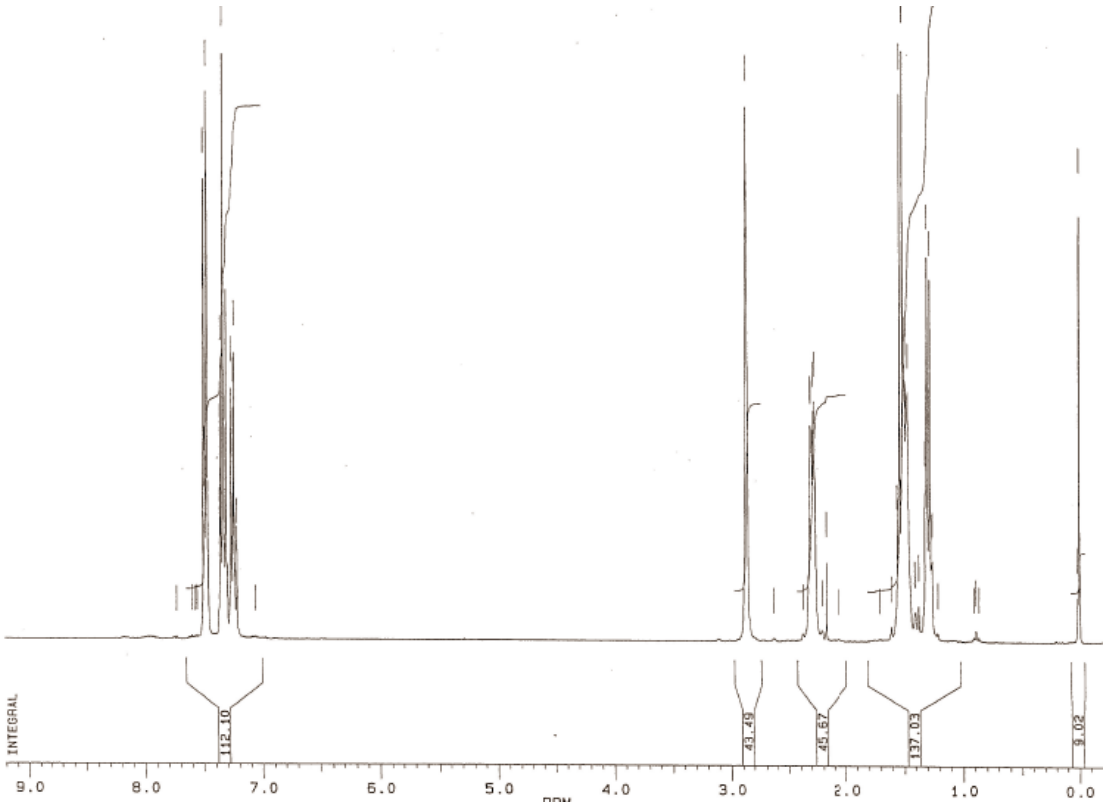

**Figure S6** Calculated (single point) rotation barriers of **5**-**N** and **6**-**N**.

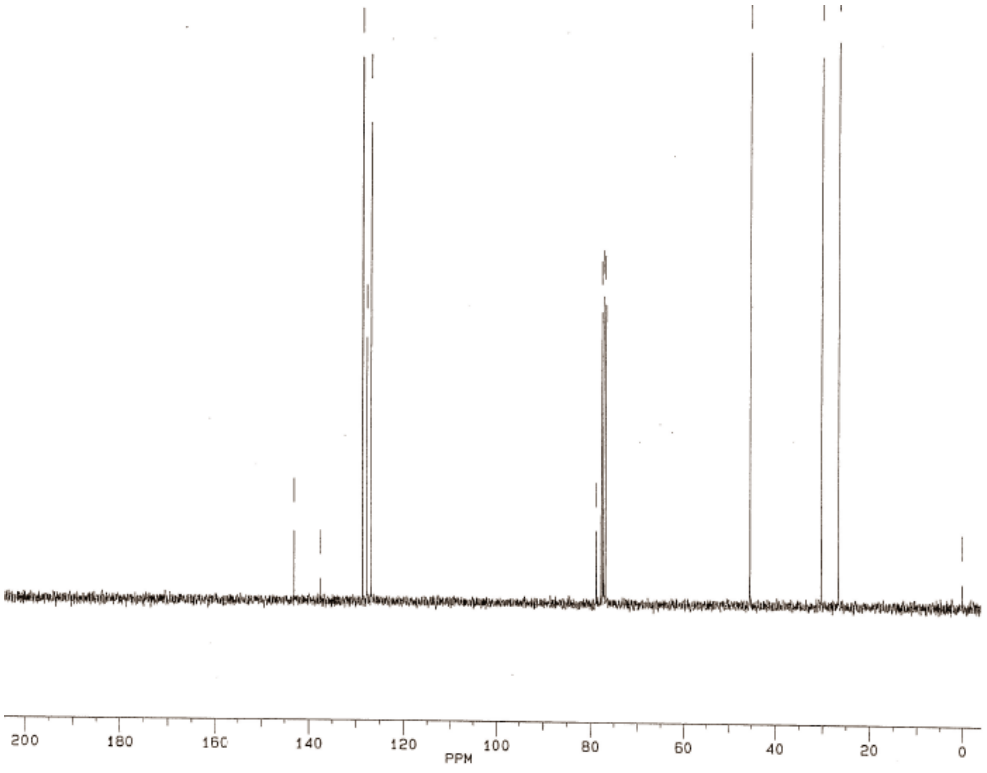
$^{1}$H-NMR and $^{13}$C- NMR spectra of compound **1**



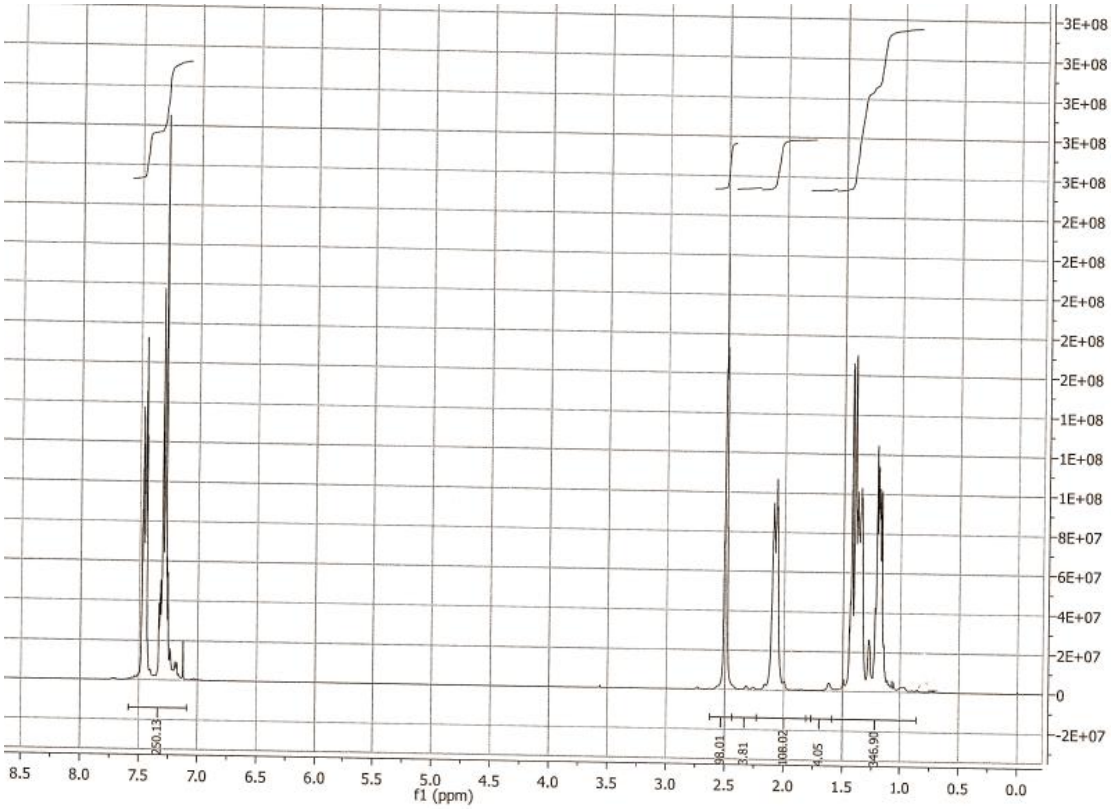



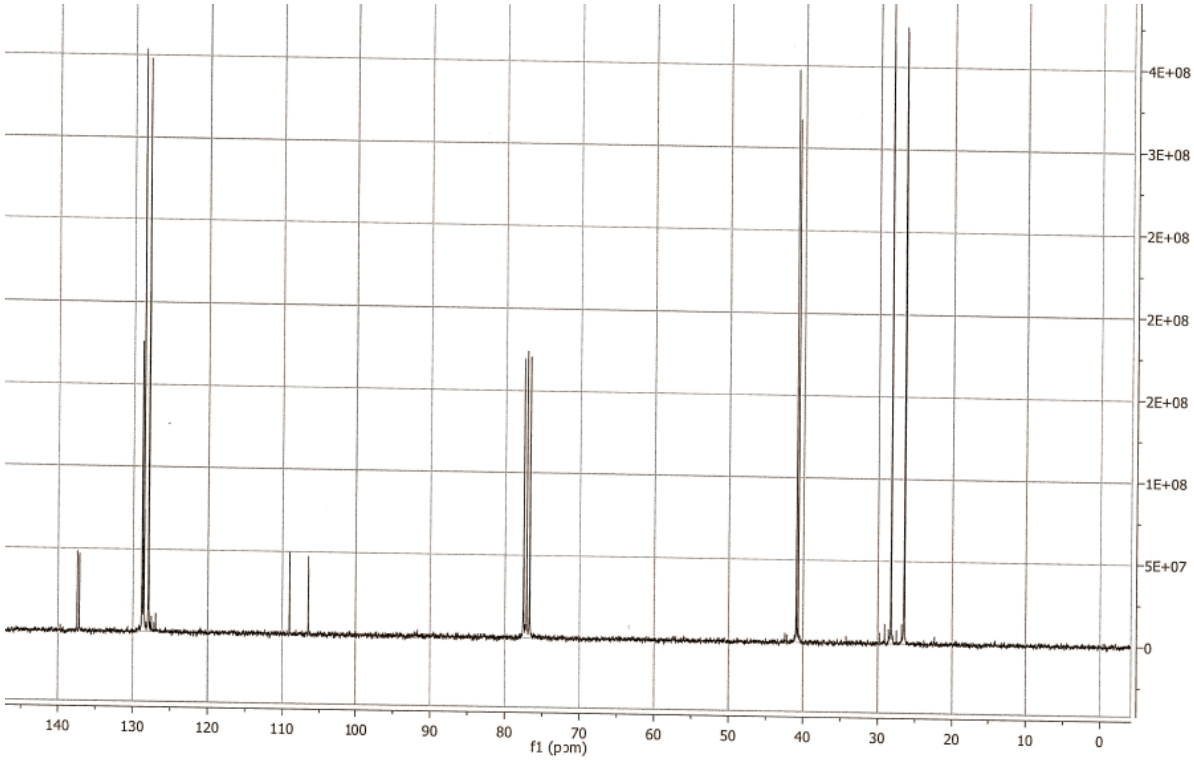
$^{1}$H-NMR and $^{13}$C- NMR spectra of compound **2**



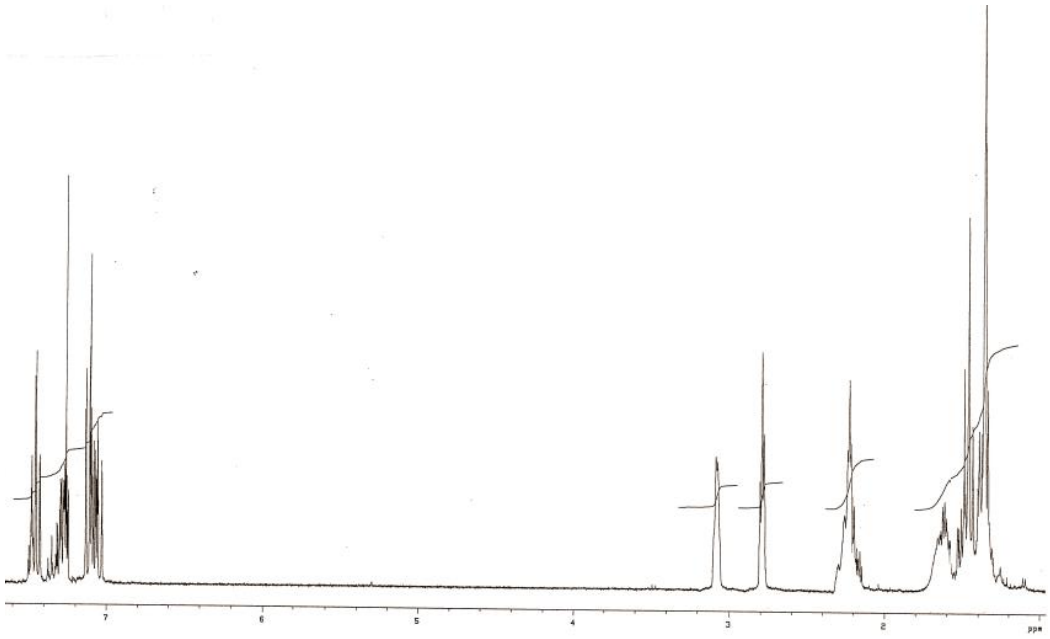



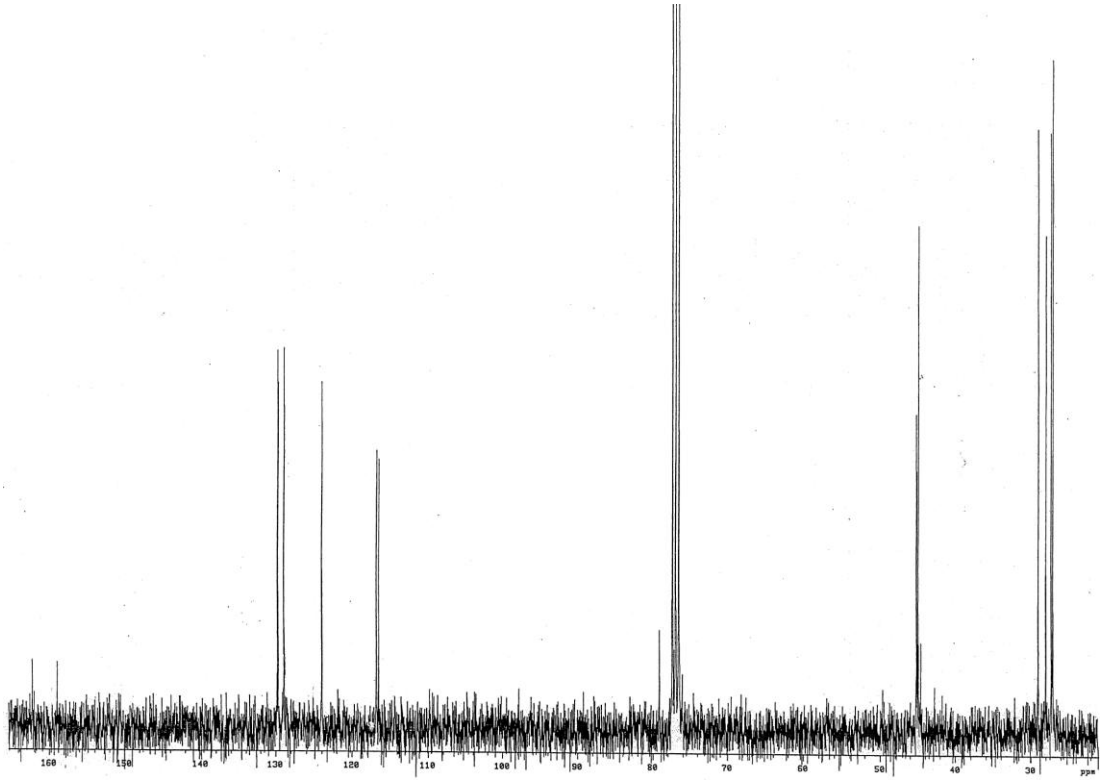
$^{1}$H-NMR and $^{13}$C- NMR spectra of compound **4**



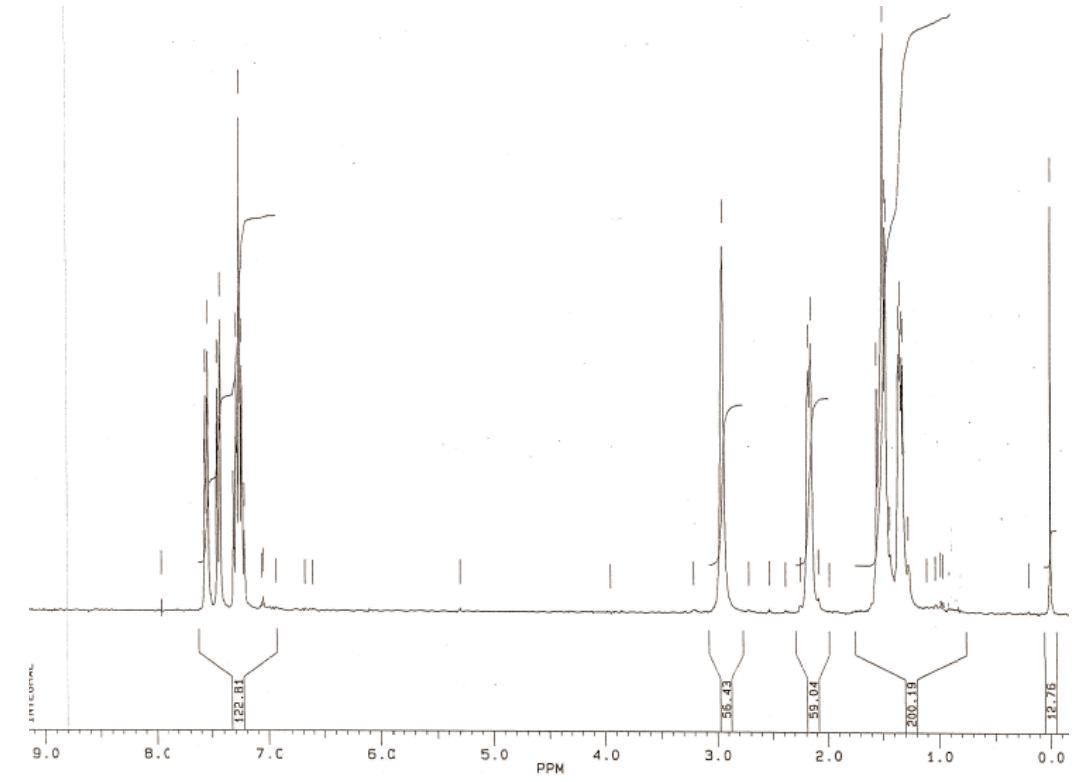



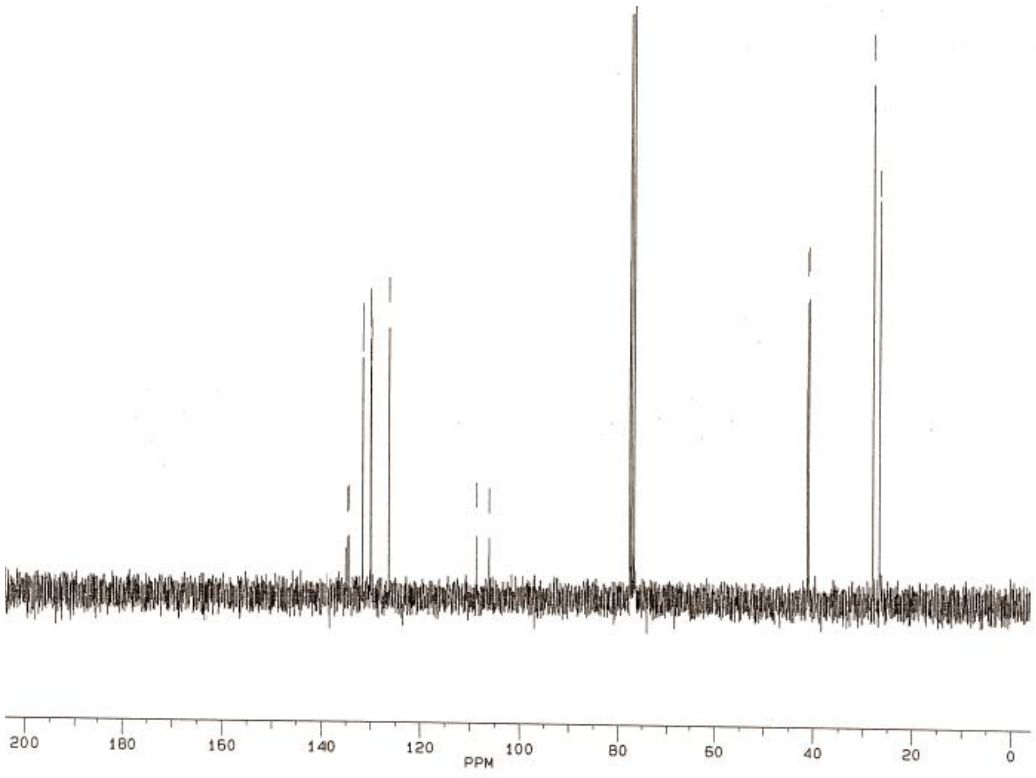
$^{1}$H-NMR and $^{13}$C- NMR spectra of compound **5**



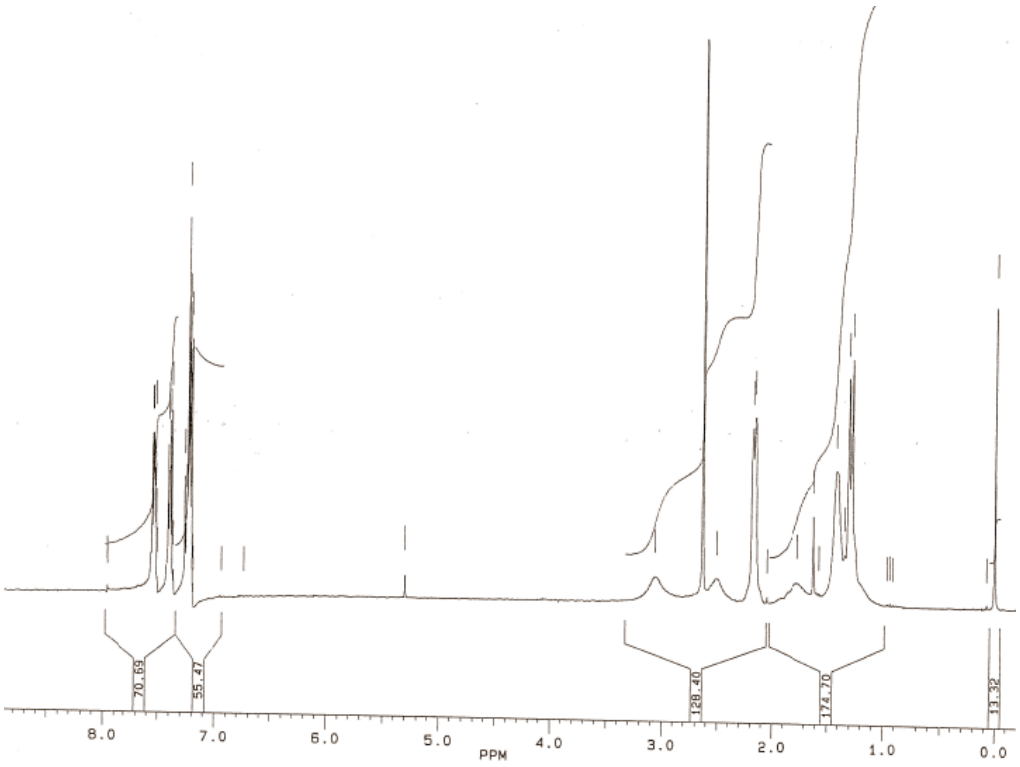


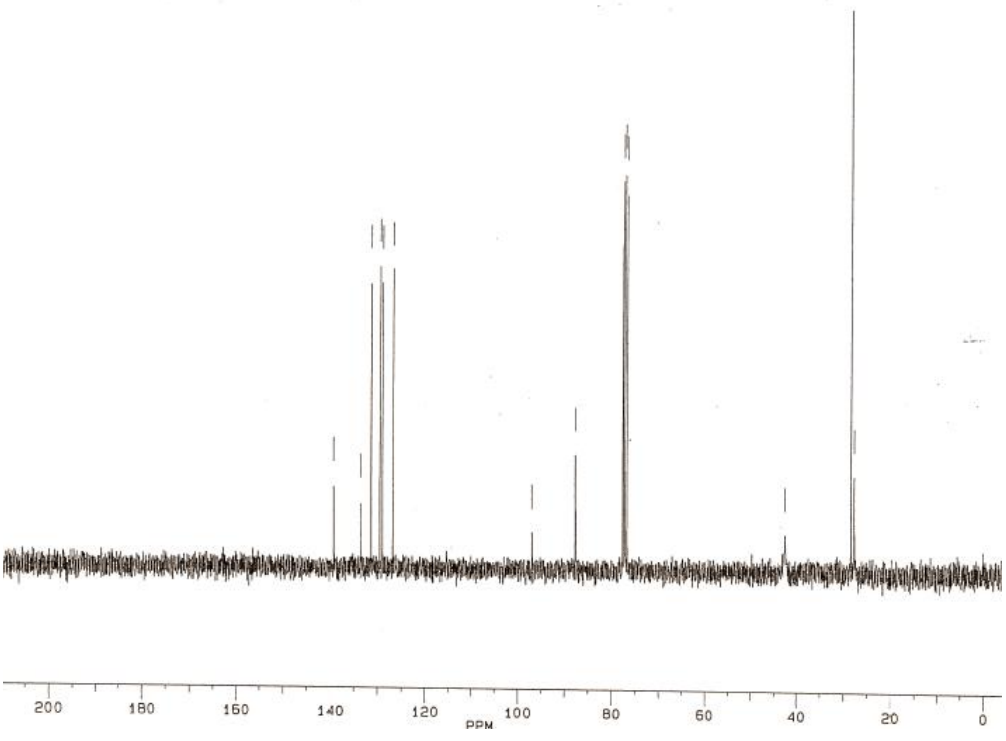
$^{1}$H-NMR and $^{13}$C- NMR spectra of compound **6**



$^{1}$H-NMR and $^{13}$C- NMR spectra of compound **9**



Cartesian coordinates (in Å) and total energies (in hartrees, ZPVE included) of all the stationary points discussed in the text. All calculations have been performed at the M06-2X/def2-TZVPP level.

**1**, E = -801.762445

| | | | |
|---|---|---|---|
| C | -2.215657000 | 1.530968000 | 0.776864000 |
| C | -0.735597000 | 1.329645000 | 1.130476000 |
| C | -0.216154000 | 0.416783000 | -0.000006000 |
| C | -0.735687000 | 1.330156000 | -1.130080000 |
| C | -2.215724000 | 1.531300000 | -0.776131000 |
| C | 0.005559000 | 2.635940000 | -0.778588000 |
| C | 0.005412000 | 2.635773000 | 0.779279000 |
| C | 1.262238000 | 0.125819000 | 0.000090000 |
| C | 1.960063000 | -0.021492000 | -1.196425000 |
| C | 3.318435000 | -0.299512000 | -1.198247000 |
| C | 4.004073000 | -0.439364000 | 0.000013000 |
| C | 3.317962000 | -0.301593000 | 1.198286000 |
| C | 1.959582000 | -0.023594000 | 1.196674000 |
| H | 1.435822000 | 0.073099000 | -2.138415000 |
| I | -1.187870000 | -1.546088000 | -0.000320000 |
| H | -2.589327000 | 2.463929000 | 1.196839000 |
| H | -2.589486000 | 2.464407000 | -1.195687000 |
| H | -0.568297000 | 0.973127000 | -2.142968000 |
| H | -0.567916000 | 0.972447000 | 2.143251000 |
| H | 1.435027000 | 0.068914000 | 2.138641000 |
| H | 3.839909000 | -0.413773000 | 2.139245000 |
| H | 5.063382000 | -0.657681000 | 0.000019000 |
| H | 3.840446000 | -0.410119000 | -2.139329000 |
| H | -0.507888000 | 3.499826000 | -1.198183000 |
| H | 1.022583000 | 2.630064000 | -1.166196000 |
| H | -0.508574000 | 3.499339000 | 1.198855000 |
| H | 1.022348000 | 2.630398000 | 1.167144000 |
| H | -2.829023000 | 0.722072000 | -1.166911000 |
| H | -2.828958000 | 0.721655000 | 1.167437000 |

**2**, E = -3078.327038

| | | | |
|---|---|---|---|
| C | -2.611456000 | 0.715958000 | 0.777022000 |
| C | -1.123197000 | 0.849908000 | 1.130215000 |
| C | -0.421743000 | 0.070121000 | -0.000021000 |
| C | -1.123313000 | 0.850437000 | -1.129812000 |
| C | -2.611535000 | 0.716285000 | -0.776520000 |
| C | -0.685508000 | 2.285040000 | -0.778532000 |
| C | -0.685360000 | 2.284651000 | 0.779562000 |
| C | 1.085797000 | 0.091325000 | -0.000019000 |
| C | 1.796726000 | 0.085920000 | -1.197053000 |
| C | 3.183505000 | 0.083645000 | -1.198730000 |
| C | 3.882151000 | 0.083533000 | 0.000056000 |
| C | 3.183430000 | 0.081604000 | 1.198810000 |
| C | 1.796663000 | 0.083878000 | 1.197053000 |
| H | 1.262844000 | 0.074225000 | -2.138052000 |
| Br | -0.931771000 | -1.852619000 | -0.000460000 |
| H | -3.183426000 | 1.541517000 | 1.198637000 |
| H | -3.183581000 | 1.541998000 | -1.197729000 |
| H | -0.878693000 | 0.536204000 | -2.141184000 |
| H | -0.878445000 | 0.535205000 | 2.141408000 |
| H | 1.262707000 | 0.070520000 | 2.137987000 |
| H | 3.718778000 | 0.075674000 | 2.138834000 |
| H | 4.963676000 | 0.081255000 | 0.000086000 |
| H | 3.718903000 | 0.079320000 | -2.138735000 |
| H | -1.376433000 | 3.015429000 | -1.196924000 |

| | | | |
|---|---|---|---|
| H | 0.308034000 | 2.502561000 | -1.166877000 |
| H | -1.376137000 | 3.014898000 | 1.198449000 |
| H | 0.308278000 | 2.501879000 | 1.167833000 |
| H | -3.025777000 | -0.211184000 | -1.165717000 |
| H | -3.025694000 | -0.211658000 | 1.165878000 |

**3,** E = -964.331942

| | | | |
|---|---|---|---|
| C | -2.803725000 | -0.158938000 | -0.730938000 |
| C | -1.351529000 | -0.543639000 | -1.052619000 |
| C | -0.543983000 | 0.323837000 | -0.065842000 |
| C | -1.311289000 | -0.176932000 | 1.176207000 |
| C | -2.775986000 | 0.090908000 | 0.802403000 |
| C | -1.057510000 | -1.689949000 | 1.064985000 |
| C | -1.101439000 | -1.947042000 | -0.470855000 |
| C | 0.952505000 | 0.118007000 | -0.036749000 |
| C | 1.672640000 | 0.413750000 | 1.118454000 |
| C | 3.048103000 | 0.250713000 | 1.158635000 |
| C | 3.728197000 | -0.207978000 | 0.038341000 |
| C | 3.022501000 | -0.494077000 | -1.120281000 |
| C | 1.644331000 | -0.329922000 | -1.156765000 |
| H | 1.152906000 | 0.787488000 | 1.991160000 |
| Cl | -0.811460000 | 2.095222000 | -0.354725000 |
| H | -3.486056000 | -0.958743000 | -1.015424000 |
| H | -3.443485000 | -0.573020000 | 1.350310000 |
| H | -1.005469000 | 0.264299000 | 2.121634000 |
| H | -1.087650000 | -0.427578000 | -2.101095000 |
| H | 1.106521000 | -0.553529000 | -2.068432000 |
| H | 3.544057000 | -0.845113000 | -2.000772000 |
| H | 4.801731000 | -0.336862000 | 0.067894000 |
| H | 3.590557000 | 0.485246000 | 2.064756000 |
| H | -1.814620000 | -2.254887000 | 1.606798000 |
| H | -0.084229000 | -1.956346000 | 1.474749000 |
| H | -1.898399000 | -2.631848000 | -0.756842000 |
| H | -0.160147000 | -2.366131000 | -0.821385000 |
| H | -3.058036000 | 1.115700000 | 1.033712000 |
| H | -3.099757000 | 0.740134000 | -1.266598000 |

**4,** E = -603.980805

| | | | |
|---|---|---|---|
| C | -1.565286000 | 1.009331000 | -0.618375000 |
| C | -0.912657000 | -0.143960000 | -0.199727000 |
| C | -1.663705000 | -1.169140000 | 0.371390000 |
| C | -3.033614000 | -1.039111000 | 0.533040000 |
| C | -3.674227000 | 0.123749000 | 0.124577000 |
| C | -2.937816000 | 1.145587000 | -0.454028000 |
| C | 0.571097000 | -0.344970000 | -0.389548000 |
| C | 1.436626000 | 0.885249000 | -0.703103000 |
| C | 2.829593000 | 0.244440000 | -0.801575000 |
| C | 2.791035000 | -0.859792000 | 0.294616000 |
| C | 1.368014000 | -0.745083000 | 0.863671000 |
| C | 1.266436000 | 0.538432000 | 1.694553000 |
| C | 1.364021000 | 1.663719000 | 0.620892000 |
| F | 0.727250000 | -1.316591000 | -1.381456000 |
| H | -1.169376000 | -2.081652000 | 0.679590000 |
| H | 3.612997000 | 0.982046000 | -0.632722000 |
| H | 3.538074000 | -0.707550000 | 1.072943000 |
| H | 1.012799000 | -1.640103000 | 1.369932000 |
| H | 1.146657000 | 1.450627000 | -1.586255000 |
| H | -1.004266000 | 1.809946000 | -1.081750000 |
| H | -3.430928000 | 2.050567000 | -0.783218000 |

| | | | |
|---|---|---|---|
| H | -4.743185000 | 0.229624000 | 0.253223000 |
| H | -3.602506000 | -1.844727000 | 0.977807000 |
| H | 2.059917000 | 0.596880000 | 2.438157000 |
| H | 0.312558000 | 0.587623000 | 2.219268000 |
| H | 2.248621000 | 2.286039000 | 0.750864000 |
| H | 0.493899000 | 2.316307000 | 0.664077000 |
| H | 2.956955000 | -1.841983000 | -0.142692000 |
| H | 2.985435000 | -0.195036000 | -1.784415000 |

**5a**, E = -1063.586307

| | | | |
|---|---|---|---|
| F | 0.927201000 | -0.571083000 | -1.845072000 |
| C | 0.768980000 | -0.289384000 | -0.486930000 |
| C | 1.557855000 | 0.978248000 | -0.111150000 |
| C | 1.472135000 | 0.940189000 | 1.420352000 |
| C | 1.536283000 | -0.582822000 | 1.743342000 |
| C | 1.659395000 | -1.229588000 | 0.358053000 |
| C | 3.051251000 | -0.933155000 | -0.211881000 |
| C | 2.982429000 | 0.583420000 | -0.531115000 |
| C | -0.721430000 | -0.418619000 | -0.200638000 |
| C | -1.659097000 | 0.605437000 | -0.060153000 |
| C | -3.004549000 | 0.335458000 | 0.173793000 |
| C | -3.455833000 | -0.967671000 | 0.245993000 |
| C | -2.556446000 | -2.008713000 | 0.070456000 |
| C | -1.221755000 | -1.724773000 | -0.146661000 |
| Cl | -1.268255000 | 2.295166000 | -0.197062000 |
| H | -0.533223000 | -2.543411000 | -0.297664000 |
| H | 3.720825000 | 1.166079000 | 0.018583000 |
| H | 3.830384000 | -1.181075000 | 0.508173000 |
| H | 1.393757000 | -2.282569000 | 0.332735000 |
| H | 1.220804000 | 1.900155000 | -0.566258000 |
| H | -3.688189000 | 1.164747000 | 0.285010000 |
| H | -4.503816000 | -1.164751000 | 0.425883000 |
| H | -2.891588000 | -3.036205000 | 0.101484000 |
| H | 2.382909000 | -0.845584000 | 2.375982000 |
| H | 0.628610000 | -0.910765000 | 2.249687000 |
| H | 2.291218000 | 1.498175000 | 1.871877000 |
| H | 0.540474000 | 1.376875000 | 1.778013000 |
| H | 3.231737000 | -1.511408000 | -1.115681000 |
| H | 3.136329000 | 0.763492000 | -1.592876000 |

**6a**, E = -1063.591140

| | | | |
|---|---|---|---|
| Cl | -0.842908000 | -1.631802000 | -1.315594000 |
| C | -0.624423000 | -0.170830000 | -0.267251000 |
| C | -1.360604000 | -0.312273000 | 1.085994000 |
| C | -1.151808000 | 1.097752000 | 1.658564000 |
| C | -1.291251000 | 2.015172000 | 0.407821000 |
| C | -1.496869000 | 1.010888000 | -0.743170000 |
| C | -2.919082000 | 0.447641000 | -0.611811000 |
| C | -2.829511000 | -0.442937000 | 0.657842000 |
| C | 0.861751000 | 0.087037000 | -0.200634000 |
| C | 1.701683000 | -0.718934000 | 0.560851000 |
| C | 3.066783000 | -0.529888000 | 0.634946000 |
| C | 3.641465000 | 0.502892000 | -0.089382000 |
| C | 2.842844000 | 1.318153000 | -0.876869000 |
| C | 1.473315000 | 1.104578000 | -0.928753000 |
| F | 1.177766000 | -1.741813000 | 1.253525000 |
| H | 0.863441000 | 1.741238000 | -1.554428000 |
| H | -3.494332000 | -0.109074000 | 1.453518000 |
| H | -3.645247000 | 1.252925000 | -0.511756000 |
| H | -1.264872000 | 1.391539000 | -1.735138000 |

| | | | |
|---|---|---|---|
| H | -1.006652000 | -1.115341000 | 1.722651000 |
| H | 3.654219000 | -1.195620000 | 1.251439000 |
| H | 4.709733000 | 0.663002000 | -0.041620000 |
| H | 3.283888000 | 2.118984000 | -1.453788000 |
| H | -2.141013000 | 2.692354000 | 0.479761000 |
| H | -0.398061000 | 2.621048000 | 0.269070000 |
| H | -1.886905000 | 1.321861000 | 2.429959000 |
| H | -0.161885000 | 1.197219000 | 2.103017000 |
| H | -3.190804000 | -0.142427000 | -1.484038000 |
| H | -3.077725000 | -1.476255000 | 0.425860000 |

**TS1**, E = -1063.571620

| | | | |
|---|---|---|---|
| C | 1.878626000 | -0.449962000 | -0.000064000 |
| C | 0.690257000 | 0.304343000 | -0.000307000 |
| C | 0.867065000 | 1.695255000 | -0.000211000 |
| C | 2.105277000 | 2.310332000 | -0.000083000 |
| C | 3.254526000 | 1.540024000 | 0.000012000 |
| C | 3.128251000 | 0.166616000 | 0.000050000 |
| C | -0.721503000 | -0.278984000 | -0.000282000 |
| C | -1.708443000 | 0.103936000 | 1.133293000 |
| C | -2.155807000 | 1.529263000 | 0.779445000 |
| C | -2.156079000 | 1.529587000 | -0.778697000 |
| C | -1.708917000 | 0.104415000 | -1.133285000 |
| C | -2.887798000 | -0.823741000 | -0.779903000 |
| C | -2.887610000 | -0.823909000 | 0.780055000 |
| F | -0.601727000 | -1.658532000 | -0.000634000 |
| H | 0.008245000 | 2.338409000 | -0.000147000 |
| Cl | 1.990168000 | -2.189353000 | 0.000198000 |
| H | -3.816615000 | -0.439792000 | 1.198723000 |
| H | -3.817047000 | -0.439971000 | -1.198355000 |
| H | -1.315990000 | -0.019891000 | -2.139781000 |
| H | -1.314958000 | -0.020673000 | 2.139532000 |
| H | 2.162313000 | 3.390088000 | -0.000042000 |
| H | 4.235260000 | 1.995213000 | 0.000113000 |
| H | 4.004718000 | -0.465079000 | 0.000204000 |
| H | -3.147415000 | 1.723274000 | -1.185884000 |
| H | -1.495968000 | 2.287068000 | -1.195257000 |
| H | -3.147071000 | 1.722589000 | 1.186982000 |
| H | -1.495733000 | 2.286696000 | 1.196145000 |
| H | -2.731981000 | -1.827459000 | -1.165740000 |
| H | -2.732135000 | -1.827745000 | 1.165720000 |

**TS2**, E = -1063.561825

| | | | |
|---|---|---|---|
| C | -1.964596000 | 0.822039000 | 0.000074000 |
| C | -0.900199000 | -0.097408000 | -0.000454000 |
| C | -1.337624000 | -1.435210000 | -0.000742000 |
| C | -2.664362000 | -1.826899000 | -0.000526000 |
| C | -3.669631000 | -0.876608000 | 0.000159000 |
| C | -3.301985000 | 0.450309000 | 0.000453000 |
| C | 0.606381000 | 0.235917000 | -0.000288000 |
| C | 1.500688000 | -0.365476000 | 1.130586000 |
| C | 1.582849000 | -1.862565000 | 0.779036000 |
| C | 1.583679000 | -1.862936000 | -0.777944000 |
| C | 1.501280000 | -0.366029000 | -1.130438000 |
| C | 2.891513000 | 0.202390000 | -0.778794000 |
| C | 2.891243000 | 0.202431000 | 0.779261000 |
| Cl | 0.818874000 | 2.032620000 | -0.000509000 |
| H | -0.622181000 | -2.229409000 | -0.001371000 |

| | | | |
|---|---|---|---|
| F | -1.803745000 | 2.150599000 | 0.000361000 |
| H | 3.671112000 | -0.434952000 | 1.192768000 |
| H | 3.671829000 | -0.434574000 | -1.192091000 |
| H | 1.159384000 | -0.147764000 | -2.139404000 |
| H | 1.158298000 | -0.146515000 | 2.139233000 |
| H | -2.900049000 | -2.882131000 | -0.000856000 |
| H | -4.713264000 | -1.159263000 | 0.000444000 |
| H | -4.031320000 | 1.248113000 | 0.001157000 |
| H | 2.501681000 | -2.287033000 | -1.181167000 |
| H | 0.766823000 | -2.438535000 | -1.204622000 |
| H | 2.500252000 | -2.286832000 | 1.183430000 |
| H | 0.765236000 | -2.437565000 | 1.205076000 |
| H | 3.034726000 | 1.203418000 | -1.173591000 |
| H | 3.034898000 | 1.203382000 | 1.174107000 |